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2. Patent application number *(The Patent Office will fill in this part)* — 0316852.3 — 18 JUL 2003

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

   Avecia Limited
   Hexagon House
   Blackley
   Manchester, M9 8ZS
   United Kingdom

   Patents ADP number *(if you know it)* — 07764137001

   If the applicant is a corporate body, give the country/state of its incorporation — GB

4. Title of the invention — Compounds, Inks and Processes

5. Name of your agent *(if you have one)* — MORPETH, Fraser Forrest

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

   Avecia Limited
   Hexagon House
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   Manchester, M9 8ZS
   United Kingdom

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Avecia Limited Authorised Signatory

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Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

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SMC 60607

APPLICANTS

AVECIA LIMITED

TITLE

COMPOUNDS, INKS AND PROCESSES

COMPOUNDS, INKS AND PROCESSES

This invention relates to new compounds, to inks, to printing processes, to printed substrates and to ink-jet printer cartridges.

Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate. The set of inks used in this technique typically comprise yellow, magenta, cyan and black inks.

With the advent of high-resolution digital cameras and ink-jet printers it is becoming increasingly common to print off photographs using an ink-jet printer. This avoids the expense of conventional silver halide photography and provides a print quickly without the need to post a film to a developing service and wait days or weeks for it to be developed and returned.

While ink-jet printers have many advantages over other forms of printing and image development there are still technical challenges to be addressed. For example, there are the contradictory requirements of providing ink colorants which are soluble in the ink medium and yet do not run or smudge excessively when printed on paper. The inks need to dry quickly to avoid sheets sticking together after they have been printed, but they should not form a crust over the tiny nozzle used in the printer. Storage stability is also important to avoid particle formation that could block the tiny nozzles used in the printer. Furthermore, the resultant images desirably do not fade rapidly on exposure to light or common oxidising gases such as ozone.

Most cyan colorants used in ink-jet printing are based on phthalocyanines and problems of fading and shade change on contact with ozone are particularly acute with dyes of this class especially when they are printed onto media containing inorganic particles, e.g. silica and/or alumina. There appears to be some aspect of the environment on the surface of such media (particularly media used for photo-realistic ink-jet printing) which promotes deterioration of these dyes in the presence of ozone.

Thus, the present invention provides a mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:

$$\mathrm{MPc}\left\langle\begin{array}{l}(\mathrm{SO_3H})_x \\ (\mathrm{SO_2NR^1R^2})_y \\ (\mathrm{SO_2NR^3LNR^4R^5})_z\end{array}\right.$$

Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

L is optionally substituted C_{1-20} alkylene, alkyenylene or alkynylene, optionally interrupted by –O-, -NH- or -S-;

R^1, R^2, R^3 and R^4 independently are H or optionally substituted C_{1-4}alkyl;

R^5 is H or an optionally substituted hydrocarbyl; or

R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

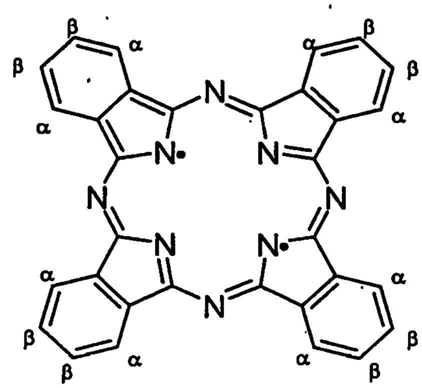
y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring.

The phthalocyanine nucleus may be represented by the bivalent radical of formula:



When a dye of Formula (1) is made by the more usual route of sulfonating a phthalocyanine pigment followed by chlorination and then amination/amidation the resultant product carries sulfo and sulfonamide/substituted sulfonamide substituents in any susceptible position.

The copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a β–position on the phthalocyanine ring may be prepared by any method known in the art, and particularly by cyclisation of appropriate β–substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable copper or nickel salt such as $CuCl_2$ followed by chlorination, amination/amidation , wherein the amine has an active substituent, and then a second amidation.

Preferably copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a β–position on the phthalocyanine ring are prepared by cyclisation of 4-sulfo-phthalic acid to phthalocyanine β tetrasulfonic acid. The phthalocyanine β tetrasulfonic acid is then chlorinated and the sulfonyl chloride

groups so formed are reacted with compounds of formula HNR^1R^2 and HNR^3X wherein R^1, R^2 and R^3 are as hereinbefore defined and X is an active leaving group, preferably halide and more preferably chloride. This reaction is preferably performed in water at a pH above 7. Typically the reaction is performed at a temperature of 30 to 70°C and is usually complete in less than 24 hours. The compounds of formula HNR^1R^2 and HNR^3X may be used as a mixture or added sequentially.

Many of the compounds of formula HNR^1R^2 and HNR^3X are commercially available, for example ammonia and 2-chloroethylamine, others may be made easily by a skilled person using methods which are well known in the art.

The $-SO_2NR^3X$ substituent on the phthalocyanine is then reacted with a compound of formula HNR^4R^5.

The ratio of sulfo to the different sulfonamide substituents may be varied by varying the nature and amount of chlorinating agent used, the relative amounts of compounds of formula HNR^1R^2 and HNR^3X used and the reaction conditions in both reactions.

When phthalocyanine β tetrasulfonic acid is an intermediate in a route to compounds of Formula (1) it may be chlorinated by reacting with any suitable chlorinating agent.

Chlorination is preferably carried out by treating the phthalocyanine β tetrasulphonic acid with chlorosulfonic acid preferably in the presence of an acid halide such as thionyl chloride, sulfuryl chloride, phosphorous pentachloride, phosphorous oxychloride and phosphorous trichloride.

M is preferably Cu.

In a first preferred embodiment R^1, R^2, R^3 and R^4 independently are H or methyl, more preferably R^1, R^2, R^3 and R^4 are all H.

In this first preferred embodiment R^5 is preferably H; optionally substituted aryl, especially optionally substituted phenyl or naphthyl; optionally substituted alkyl, especially optionally substituted C_{1-4}-alkyl or optionally substituted heterocycyl. More preferably R^5 is phenyl, especially phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents. It is especially preferred that R^5 is phenyl bearing a single sulfo, carboxy or phosphato substituent, particularly phenyl bearing a single sulfo substituent.

In a second preferred embodiment R^1, R^2 and R^3 independently are H or methyl, more preferably R^1, R^2 and R^3 are all H.

In the second preferred embodiment R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted mono, bi or tricyclic aliphatic or aromatic ring. More preferably R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted 3 to 8 membered aliphatic or aromatic ring. It is especially preferred that R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic

ring. The optionally substituted aromatic or aliphatic ring formed by R^4 and R^5 together with the nitrogen atom to which they are attached may comprise at least one further hetero atom. Examples of preferred ring systems include imidazole, pyrazole, pyrrole, benzimidazole, indole, tetrahydro(iso)quinoline, decahydro(iso)quinoline, pyrrolidine, pyrroline, imidazolidine, imidazoline, pyrazolidine, pyrazoline, piperidine, piperazine, indoline, isoindoline, thiazolidine and morpholine. Particularly morpholine.

L is preferably optionally substituted C_{1-20} alkylene optionally interrupted by –O-, -NH- or -S-, more preferably L is optionally substituted C_{1-12} alkylene optionally interrupted by –O-, -NH- or -S-. It is especially preferred that L is optionally substituted C_{1-8} alkylene optionally interrupted by –O-, -NH- or -S-, more especially L is optionally substituted C_{1-4} alkylene optionally interrupted by –O-, -NH- or -S-. It is particularly preferred that L is optionally substituted C_{1-4} alkylene, more particularly L is $-CH_2-CH_2-$.

Preferred optional substituents which may be present on R^1, R^2, R^3, R^4, R^5 and L may be independently selected from: optionally substituted alkyl (preferably C_{1-4}-alkyl), optionally substituted alkoxy (preferably C_{1-4}-alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene oxide or polypropylene oxide), carboxy, phosphato, sulpho, nitro, cyano, halo, ureido, $-SO_2F$, hydroxy, ester, $-NR^aR^b$, $-COR^a$, $-CONR^aR^b$, $-NHCOR^a$, carboxyester, sulphone, and $-SO_2NR^aR^b$, wherein R^a and R^b are each independently H or optionally substituted alkyl (especially C_{1-4}-alkyl). Optional substituents for any of the substituents described for R^1, R^2, R^3, R^4, R^5 and L may be selected from the same list of substituents.

Preferably x has a value of 0.5 to 3.5.

Preferably y has a value of 0.5 to 3.5.

Preferably z has a value of 0.5 to 3.5.

The compounds of Formula (1) are also preferably free from fibre reactive groups. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of fibre reactive groups excluded from the compounds of Formula (1) there may be mentioned aliphatic sulfonyl groups which contain a sulfate ester group in beta-position to the sulfur atom, e.g. beta-sulfato-ethylsulfonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids, for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of vinylsulfonyl- or beta-chloroethylsulfonyl- or beta-sulfatoethyl-sulfonyl-endo- methylene cyclohexane carboxylic acids. Other examples of

cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl carbonyl; activated halogenated 1,3-dicyanobenzene radicals; and heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms in the heterocyclic ring and at least one cellulose reactive substituent on a carbon atom of the ring, for example a triazinyl halide.

In view of the above preferences a preferred a mixture of copper phthalocyanine dyes of Formula (1) is of Formula (2) and salts thereof:

$$\mathrm{MPc}\left\langle\begin{array}{l}(\mathrm{SO_3H})_x \\ (\mathrm{SO_2NR^1R^2})_y \\ (\mathrm{SO_2NR^3L^1NR^6R^7})_z\end{array}\right.$$

Formula (2)

wherein:

M Cu or Ni;

Pc represents a phthalocyanine nucleus;

L^1 is optionally substituted C_{1-8} alkylene optionally interrupted by –O-, -NH- or -S-;

R^1, R^2, R^3 and R^6 independently are H or optionally substituted C_{1-4}alkyl;

R^7 is H, optionally substituted aryl, optionally substituted alkyl or optionally heterocycyl; or

R^6 and R^7 together with the nitrogen atom to which they are attached represent an optionally substituted 5 or 6 membered aliphatic or aromatic ring;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring.

A more preferred mixture of copper phthalocyanine dyes of Formula (1) is of Formula (3) and salts thereof:

$$\mathrm{CuPc}\left\langle\begin{array}{l}(\mathrm{SO_3H})_x \\ (\mathrm{SO_2NR^1R^2})_y \\ (\mathrm{SO_2NR^3L^2NR^8R^9})_z\end{array}\right.$$

Formula (3)

wherein:

Pc represents a phthalocyanine nucleus;

L^2 is optionally substituted C_{1-4} alkylene;

R^1, R^2, R^3 and R^8 independently are H or optionally substituted C_{1-4}alkyl;

R^9 is H or phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents; or

R^8 and R^9 together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6- membered aliphatic or aromatic ring;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring.

In mixtures of compounds of Formula (2) and Formula (3) preferences for R^1, R^2, R^3, x, y and z are as for Formula (1) and are as described above.

In mixtures of compounds of Formula (2) and Formula (3) preferences for L^1 and L^2 are as described above for L.

In mixtures of compounds of Formula (2) and Formula (3) preferences for R^6 and R^8 are as for R^4 and preferences for R^7 and R^9 are as for R^5 above in the first preferred embodiment of the invention. Preferences for R^6 and R^8, and R^7 and R^9 are as for R^4 and R^5 respectivelyuin the second preferred embodiment.

Acid or basic groups on the compounds of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and in salt form.

Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as $((CH_3)_4N^+)$ and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted into a salt using known techniques.

The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

When the preferred route, as set out above, is used to synthesise compounds of Formula (1) are largely ammonium salts. However, any known techniques may be used to exchange ammonia for another cation for example, acidification optionally followed by dialysis, to remove the original cations with subsequent addition of the alternative cations. Use of ion exchange resins and reverse osmosis are amongst the other well-known techniques for exchanging one cation for another.

The compounds of Formula (1) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good

balance of solubility, storage stability and fastness to water and light. In particular they display excellent light and ozone fastness.

According to a second aspect of the present invention there is provided a composition comprising a compound according to the first aspect of the invention and a liquid medium.

Preferred compositions comprise:

(a) from 0.01 to 30 parts of a compound according to the first aspect of the invention; and

(b) from 70 to 99.99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and organic solvent and organic solvent free from water. Preferably the liquid media comprises a mixture of water and organic solvent or organic solvent free from water.

When the medium (b) comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C_{1-6}-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C_{1-4}-alkyl ethers of diols, preferably mono-C_{1-4}-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone;

cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C_{1-4}-alkyl and C_{1-4}-alkyl ethers of diols, more preferably mono- C_{1-4}-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH_2Cl_2; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of polar solvents include C_{1-4}-alcohols.

In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C_{1-4}-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may of course contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I. Direct

Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

It is preferred that the composition according to the invention is an ink suitable for use in an ink-jet printer. Ink suitable for use in an ink-jet printer is an ink which is able to repeatedly fire through an ink-jet printing head without causing blockage of the fine nozzles.

The inks may be incorporated in an ink-jet printer as a high concentration cyan ink, a low concentration cyan ink or both a high concentration and a low concentration ink. In the latter case this can lead to improvements in the resolution and quality of printed images. Thus the present invention also provides a composition according to the third aspect of the present invention (preferably an ink) where component (a) is present in an amount of 2.5 to 7 parts, more preferably 2.5 to 5 parts (a high concentration ink) or component (a) is present in an amount of 0.5 to 2.4 parts, more preferably 0.5 to 1.5 parts (a low concentration ink).

An ink suitable for use in an ink-jet printer preferably has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C.

An ink suitable for use in an ink-jet printer preferably contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a colorant of Formula (1) or any other component of the ink).

Preferably an ink suitable for use in an ink-jet printer has been filtered through a filter having a mean pore size below 10µm, more preferably below 3µm, especially below 2µm, more especially below 1µm. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

Preferably an ink suitable for use in an ink-jet printer contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

A third aspect of the invention provides a process for forming an image on a substrate comprising applying an ink according to the second aspect of the invention thereto by means of an ink-jet printer.

The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as

described in International Patent Application WO00/48938 and International Patent Application WO00/55089.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Glossy papers are especially preferred.

A fourth aspect of the present invention provides a material preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers printed with a compound according to the first aspect of the invention, a composition according to the second aspect of the invention or by means of a process according to the third aspect of the invention.

It is especially preferred that the printed material of the third aspect of the invention is a photograph printed using an ink-jet printer.

A fifth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the second aspect of the present invention. The cartridge may contain a high concentration ink and a low concentration ink, as described in the second aspect of the invention, in different chambers.

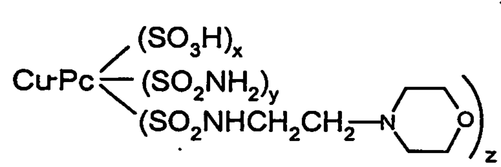
The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

<u>Example 1</u>

<u>Analysis of phthalocyanines</u>

Conformation of the structure of compounds of Formula (1) is by mass spec. Elemental analysis is used to determine the ratios of x to y + z. Thus, when the sum of x plus y and z is not exactly 4 this is due to the presence of impurities. The presence of these impurities and their effect on the estimated values of x , y and z would be well known to a person skilled in the art who would appreciate that the value of x plus y plus z will not exceed 4 and who would treat the experimentally determined values of x, y and z as indicative of the true ratios of the groups.

<u>Preparation of: the following dye substituted only in the β-position where x is 1.2 and (y + z) is 3.2:</u>



Stage 1

The following components; potassium 4-sulphophthalic acid (56.8g), urea (120g), $CuCl_2$ (6.9g), ammonium molybdate (1.2g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.5g) were mixed in a reaction vessel.

The mixture was then warmed in stages (130°C/30 minutes, 150°C/30 minutes,180°C/30 minutes, 220°C) over 2 hours and the melt which formed was stirred at 220°C for a further 2 hours.

The solid which formed was extracted 4 times with hot water (4 x 200ml) and the extract was filtered to remove insoluble material.

The resultant filtrate was stirred at between 60°C – 70°C and then sufficient sodium chloride was added to give 7% brine solution. Stirring was continued and the solid which precipitated was filtered, washed with a 10% brine solution (200 ml) and pulled dry by vacuum. The resultant damp solid (77.6g) was slurried in acetone, filtered and dried first at room temperature and then at 50°C. Analysis revealed 3.8 sulfo groups per phthalocyanine.

Stage 2 - Preparation of:

$$\mathrm{CuPc}\begin{cases}(\mathrm{SO_3H})_x\\(\mathrm{SO_2NH_2})_y\\(\mathrm{SO_2NHCH_2CH_2Cl})_z\end{cases}$$

Phosphorous oxychloride (5.84g) was added dropwise to chlorosulfonic acid (54.3g)while keeping the reaction temperature below 30°C. The sulfonated phthalocyanine product of stage 1 (21g) was then added to this mixture over 10-15 minutes while keeping temperature below 60°C. This reaction mixture was stirred at 60°C for 10-15 minutes and then slowly heated to 138°C to 140°C and kept at this temperature, with stirring for 3 hours. At the end of this time the reaction mixture was cooled and stirred at room temperature overnight. The next day the reaction-melt was drowned onto a mixture of water/ice/salt/HCl (100ml/200g/4g/mlml), keeping the temperature below 0°C using external cooling and further addition of ice as necessary. The resultant suspension was stirred at 0°C for 20 minutes and then filtered, washed with acidified solution of ice cold 10% brine solution (100 ml) and pulled dry by vacuum to give a damp paste. This paste was then added in portions to a solution comprising 2-chloroethylamine hydrochloride (5.5g), water (200ml) and ice (100g). The pH of the resultant suspension was adjusted to pH 7 with concentrated ammonia and then stirred at 10° to 20°C at pH 7 to 7.5 for 3 hours. At the end of this time the reaction mixture was warmed to 37°- 40°C, adjusted to pH 7.5 with concentrated ammonia and stirred for 1 hour 30 minutes. The mixture was

then stirred at room temperature overnight. The next day the reaction mixture was warmed to 40°C and stirred for 30 minutes. The pH of the reaction mixture was adjusted to less than 1 with concentrated HCl and NaCl was added to 10% brine with stirring. The precipitate which formed was filtered, washed with acidified 20% brine solution and pulled dry with a vacuum pump. The solid was filtered, pulled dry with a vacuum pump and dried at room temperature to give 17.2g of product.

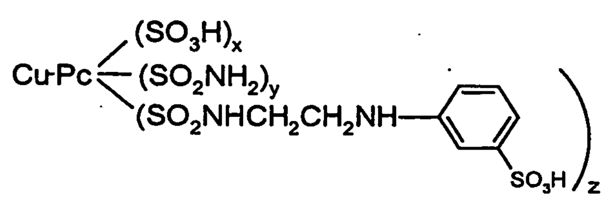
Stage 3

Preparation of the title product

The product of stage 2 (8g) was mixed with 3.26g of morpholine in 250 ml of water. This mixture was stirred at 60° to 70°C while the pH was maintained above pH10 by the addition of 2M NaOH. After 1 hour there were no further changes in the pH and the mixture was then stirred for a further 3 hours. The reaction mixture was then filtered and the filtrate (300 ml) was adjusted to pH 6.5 with concentrated HCl and Na Cl added to give a 10% solution. This mixture was stirred and the precipitate which formed was filtered, washed with 100ml of a 10% NaCl solution at pH 2 and then pulled as dry as possible with a vacuum pump. The solid was then slurried in 200 ml of deionised water at pH = 8.5 (pH adjusted with NaOH), dialysed to low conductivity versus water and dried at 70°C to give 6.7g of product.

Example 2

Preparation of: the following dye substituted only in the Beta position wherein x is 1.3 and (y + z) is 2:



Stages 1 and 2 were carried out as described above for Example 1

Stage 3

Preparation of the title product

The product of stage 2 (5.5g) was mixed with 4.33g of metanilic acid in 150 ml of deionised water. This mixture was adjusted to pH9.8 and warmed with stirring to 70°C while the pH was maintained above pH9.5 by the addition of 2M NaOH. The mixture was then stirred for a further 3 hours. The reaction mixture was then adjusted to pH 8 with concentrated HCl, allowed to cool to 40°C and then NaCl was added to give a 15% solution. This mixture was stirred and the precipitate which formed was filtered, washed with 100ml of a 20% NaCl solution and then pulled as dry as possible with a vacuum

pump. The solid was then dissolved in deionised water, dialysed to low conductivity versus water and dried at 70°C to give 5g of product.

Preparation of inks:

Inks of the present invention may be prepared by dissolving 3.5g of the compounds of Example 1 and Example 2 in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Further Inks

The inks described in Tables A and B may be prepared using the compounds made in Example 1 and 2. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

PG = propylene glycol
DEG = diethylene glycol
NMP = N-methyl pyrollidone
DMK = dimethylketone
IPA = isopropanol
MEOH = methanol
2P = 2-pyrollidone
MIBK = methylisobutyl ketone
P12 = propane-1,2-diol
BDL = butane-2,3-diol
CET= cetyl ammonium bromide
PHO = Na_2HPO_4 and
TBT = tertiary butanol
TDG = thiodiglycol

TABLE A

Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
1	10.0	85	3		3	3				5	1	
2	2.1	91		8								1
1	3.1	86	5					0.2	4			5
2	1.1	81			9		0.5	0.5			9	
1	2.5	60	4	15	3	3			6	10	5	4
2	5	65		20					10			
1	2.4	75	5	4		5				6		5
2	4.1	80	3	5	2	10		0.3				
1	3.2	65		5	4	6			5	4	6	5
2	5.1	96								4		
1	10.8	90	5						5			
2	10.0	80	2	6	2	5			1		4	
1	1.8	80		5							15	
2	2.6	84			11						5	
1	3.3	80	2			10				2		6
2	12.0	90				7	0.3		3			
1	5.4	69	2	20	2	1					3	3
2	6.0	91			4						5	

TABLE B

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
2	9.0	90		5						1.2		5
1	1.5	85	5	5		0.15	5.0	0.2				
2	2.5	90		6	4					0.12		
1	3.1	82	4	8		0.3						6
2	0.9	85		10					5	0.2		
1	8.0	90		5	5			0.3				
2	4.0	70		10	4				1		4	11
1	2.2	75	4	10	3				2		6	
2	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	5	
2	5.0	78	5	11							6	
1	5.4	86			7						7	
2	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
1	2.0	90		10								
2	2	88						10				
1	5	78			5			12			5	
2	8	70	2		8			15			5	
1	10	80						8			12	
2	10	80		10								

CLAIMS

1. A mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:

$$MPc \left\langle \begin{array}{l} (SO_3H)_x \\ (SO_2NR^1R^2)_y \\ (SO_2NR^3LNR^4R^5)_z \end{array} \right.$$

Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

L is optionally substituted $C_{1\text{-}20}$ alkylene, alkyenylene or alkynylene, optionally interrupted by –O-, -NH- or -S-;

R^1, R^2, R^3 and R^4 independently are H or optionally substituted $C_{1\text{-}4}$alkyl;

R^5 is H or an optionally substituted hydrocarbyl; or

R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring.

2. A mixture of copper phthalocyanine dyes according to claim 1 wherein M is Cu.

3. A mixture of copper phthalocyanine dyes according to either claim 1 or claim 2 wherein R^1, R^2, R^3 and R^4 independently are H or methyl and R^5 is H, optionally substituted aryl, optionally substituted alkyl or optionally substituted heterocycyl.

4. A mixture of copper phthalocyanine dyes according to claim 3 wherein R^5 is phenyl bearing at least one sulfo, carboxy or phosphato substituent and having further optional substituents.

5. A mixture of copper phthalocyanine dyes according to either claim 1 or claim 2 wherein R^1, R^2 and R^3 independently are H or methyl and R^4 and R^5 together with the

nitrogen atom to which they are attached represent an optionally substituted mono, bi or tricyclic aliphatic or aromatic ring.

6. A mixture of copper phthalocyanine dyes according to claim 5 wherein R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted 5- or 6-membered aliphatic or aromatic ring.

7. A mixture of copper phthalocyanine dyes according to any one of the preceding claims of Formula (2) and salts thereof:

$$\mathrm{MPc}\left\langle\begin{array}{l}(SO_3H)_x \\ (SO_2NR^1R^2)_y \\ (SO_2NR^3L^1NR^6R^7)_z\end{array}\right.$$

Formula (2)

wherein:

M Cu or Ni;

Pc represents a phthalocyanine nucleus;

L^1 is optionally substituted C_{1-8} alkylene optionally interrupted by –O-, -NH- or -S-;

R^1 , R^2, R^3 and R^6 independently are H or optionally substituted C_{1-4}alkyl;

R^7 is H, optionally substituted aryl, optionally substituted alkyl or optionally heterocycyl; or

R^6 and R^7 together with the nitrogen atom to which they are attached represent an optionally substituted 3 to 8 membered aliphatic or aromatic ring;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring.

8. A composition comprising a compound according to any one of claims 1 to 7 and a liquid medium.

9. A composition according to claim 8 comprising

(c) from 0.01 to 30 parts of a compound according to any one of claims 1 to 7; and

(d) from 70 to 99.99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

10. A composition according to either claim 8 or claim 9 which is an ink suitable for use in an ink jet printer.

11. A process for forming an image on a substrate comprising applying an ink according to claim 10 thereto by means of an ink-jet printer.

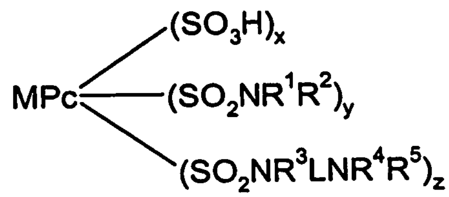
12. A material printed with a composition according to any one of claims 8 10 or a compound according to any one of claims 1 to 7 or by a process according to claim 11.

13. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in claim 10.

ABSTRACT

COMPOUNDS, INKS AND PROCESSES

A mixture of copper phthalocyanine dyes of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus;

L is optionally substituted C_{1-20} alkylene, alkyenylene or alkynylene, optionally interrupted by –O-, -NH- or -S-;

R^1, R^2, R^3 and R^4 independently are H or optionally substituted C_{1-4}alkyl;

R^5 is H or an optionally substituted hydrocarbyl; or

R^4 and R^5 together with the nitrogen atom to which they are attached represent an optionally substituted aliphatic or aromatic ring system;

x is 0.1 to 3.8;

y is 0.1 to 3.8;

z is 0.1 to 3.8;

the sum of (x+y+z) is 4;and

the substituents, represented by x, y and z, are attached only to a β-position on the phthalocyanine ring. Also novel compositions and inks, ink-jet printing processes, printed images and cartridges.